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14. ABSTRACT The dissociative recombination of Na ⁺ (D ₂ O) ion has been studied at the heavy-ion storage ring CRYRING (Manne Siegbahn Laboratory, Stockholm University). The cross section has been measured as a function of center-of-mass energy ranging from 1 meV to 0.1eV and found to have an E ^{-1.37} dependence. The rate coefficient has been deduced to be $(2.3 \pm 0.32) \times 10^{-7} (T_e/300)^{-0.95 \pm 0.01} \text{ cm}^3 \text{ s}^{-1}$ for T _e = 50–1000 K. The branching ratios have been measured at 0 eV. Of the four energetically accessible dissociation channels, three channels are found to occur although the channel that breaks the weak Na ⁺ -D ₂ O bond is by far dominant.						
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Dissociative recombination study of $\text{Na}^+(\text{D}_2\text{O})$ in a storage ring

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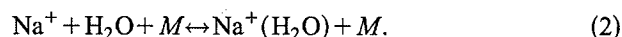
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I. INTRODUCTION

Easily ionizable alkali metals emitted from surfaces can contribute significantly to the plasma that forms around hypersonic ($>\text{Mach } 5$) vehicles during atmospheric reentry. Due to the high pressure of atmospheric gases around the vehicle and the low radiative recombination rate of alkali atomic ions, plasma neutralization is dominated by three-body processes, e.g.,



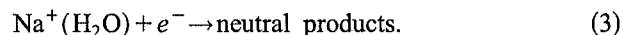
where M is an atmospheric gas or an electron. Alternatively, a third body can increase the recombination rate through a chaperone mechanism, which takes place in two steps. The alkali ion first clusters to an atmospheric gas molecule such as water,



Although it might be instructive to consider clustering to the most abundant atmospheric species, N_2 and O_2 , $\text{Na}^+(\text{H}_2\text{O})$ is expected to be more abundant than the $\text{Na}^+ \cdot \text{N}_2$ and $\text{Na}^+ \cdot \text{O}_2$ complexes due to much stronger binding energy in $\text{Na}^+(\text{H}_2\text{O})$.^{1,2} The interaction between Na^+ and water has been the subject of numerous experimental^{3,4} and theoretical^{5–14} studies due to its important role in many chemical and biochemical phenomena. The formation of $\text{Na}^+(\text{H}_2\text{O})$ in the presence of a third body [reaction (2)] proceeds in two-step collision processes, where the first step is water attachment to the ion, after which the cluster is left unstable, and the second step is removing excess energy by means of collision with the third body,¹⁵ i.e., the well known Lindeman mechanism for association. The formation of

$\text{Na}^+(\text{H}_2\text{O})$ may also result from rapid ligand switching from $\text{Na}^+(\text{N}_2)$ or $\text{Na}^+(\text{CO}_2)$. This is certainly the case in the atmosphere for $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ formation from $\text{H}_3\text{O}^+(\text{N}_2)$.¹⁶

The second step in the chaperone mechanism involves the ionic cluster recombining with a free electron,



This is called dissociative recombination (DR) and is usually much faster than the three-body process shown in reaction (1). The equilibrium constant for reaction (2) is known³ but the rate for DR of $\text{Na}^+(\text{H}_2\text{O})$ [reaction (3)] is not. Here, we report a study of reaction (3) made at the heavy-ion storage ring CRYRING to better assess the importance of the chaperone mechanism. In order to better obtain product distributions, $\text{Na}^+(\text{D}_2\text{O})$ was used to compensate for the low resolution of the detector. The isotopic shifts in the geometry, rate constants and branching ratios are expected to be small based on previous experience with systems of similar size.

The dissociative recombination of $\text{Na}^+(\text{H}_2\text{O})$ is also relevant to the chemistry of the D-region of the ionosphere, where a 10 km half-width Na^+ belt is present centered near 93 km altitude,¹⁷ and to the formation of sporadic sodium layers, which can occur at the altitudes between 90 and 105 km.^{18,19} Moreover, positive ions of mass 41 amu, presumably $\text{Na}^+(\text{H}_2\text{O})$, have been observed with a rocket-borne mass spectrometer at an altitude of 82 km.²⁰ Similar considerations as discussed above apply to this situation, i.e., Na^+ cannot recombine but the water cluster would.

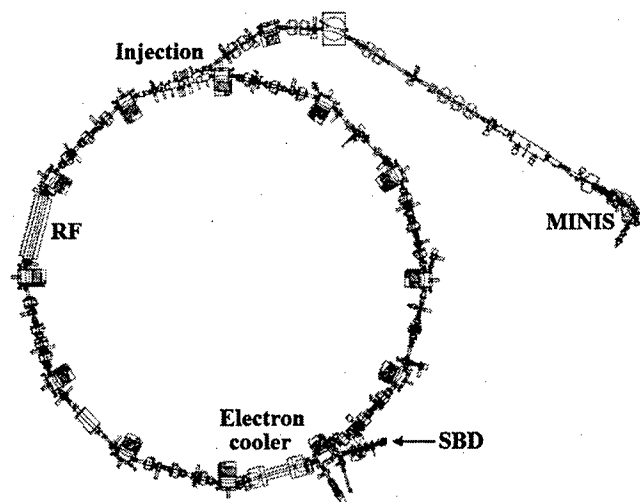
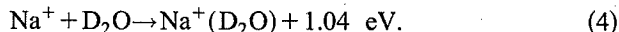


FIG. 1. Layout of the heavy-ion storage ring CRYRING at Manne Siegbahn Laboratory, Stockholm.

II. EXPERIMENT

Experiments were performed at the heavy-ion storage ring CRYRING located at Manne Siegbahn Laboratory, Stockholm University, Sweden. A detailed description of the experimental setup can be found elsewhere.²¹ The layout of CRYRING, which is 51.6 m in circumference, is shown in Fig. 1. The ions were produced in a hot filament ion source (MINIS) by mixing Na from evaporated NaCl with D₂O:



Deuterated NaOD and Na⁺(D₂O) are known to have the same structure,²² for which the geometry is shown in Fig. 2.¹⁴ Once formed in the source, the ions were extracted at 40 keV, mass selected and injected into the ring where the beam was further accelerated by a radio frequency (rf) cavity to the maximum beam energy, $E_b = 2.19 \text{ MeV}$, which was limited by the magnetic rigidity of the storage ring.²³ The data acquisition was started 1 s after the ion injection, which ensured infrared vibrational relaxation of the ions to a thermal distribution of vibrational states. The interaction between ions and a high-density electron beam having a current of 0.4 mA occurred over a length of 0.85 m in the electron cooler. The electron velocities in the center-of-mass frame are characterized by a flattened Maxwellian distribution with parallel and transverse temperatures of $kT_{\parallel} = 0.1 \text{ meV}$ and $kT_{\perp} = 2 \text{ meV}$, respectively.²⁴ The neutral particles arising from dissociative recombination and collisions with rest gas mol-

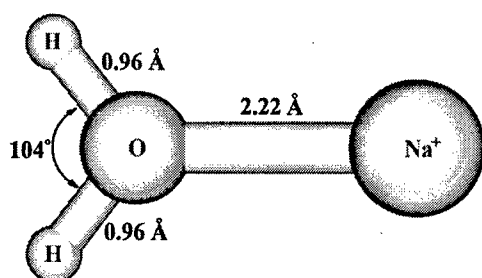


FIG. 2. Geometric structure of Na⁺(H₂O).

ecules were separated from the charged particles in the dipole magnet after the electron cooler, and were detected by an ion-implanted surface barrier detector (SBD) with 3000 mm² active area located at a distance of 3.85 m from the midpoint of the electron cooler. The output signal from the detector was amplified, shaped, and recorded by a multichannel analyzer (MCA) giving a pulse-height spectrum showing the number of counts versus the energy of the incoming particle. Since all fragments travel with the ion beam velocity, the energy of the individual neutral particles, E_n can be expressed as

$$E_n = m_n / m_{\text{Na}^+(\text{D}_2\text{O})} \times E_b, \quad (5)$$

where m_n is the mass of the fragment and $m_{\text{Na}^+(\text{D}_2\text{O})}$ is the mass of the parent ion. Particles from the same recombination event hit the detector simultaneously for our purposes.

The pressure in the storage ring was low ($\sim 10^{-11}$ Torr) which ensured a small number of collisions with the background gas and resulted in a lifetime of the ion beam of 5.6 s. This background was measured and the data corrected accordingly. The cycle time was chosen to be 7.7 s, which included ion injection and acceleration (1 s), vibrational relaxation of the ions (1 s), data acquisition (3 s), and resetting of the ring (2.7 s).

III. DATA ANALYSIS PROCEDURE

A. Dissociative recombination cross section and rate coefficient measurements

The collision energy in the center-of-mass frame can be defined as

$$\sqrt{E_{cm}} = \sqrt{qU_{cath}} - \sqrt{E_{cool}}, \quad (6)$$

where q is the elementary charge, U_{cath} is the effective cathode voltage at which the electrons are produced, and E_{cool} is the electron beam energy when the average velocities of two beams are matched, which quantitatively equals the value $(m_e / m_{\text{Na}^+(\text{D}_2\text{O})}) E_b = 31.3 \text{ eV}$, where m_e is the electron mass. We have denoted the subscript "cool," because at these conditions for lighter ions a cooling process is observed resulting in quenching of the energy spread of the ions by means of Coulomb interactions. For detailed description of the electron cooling see Ref. 24. For an ion as heavy as Na⁺(D₂O), cooling is not very effective.

The measurement for the DR cross section versus the interaction energy was performed by linearly ramping the cathode voltage from 43.5 to 21.2 V, covering the range of collision energy between 0 and 1 eV twice [Fig. 3(a)]. In order to count the number of DR events, the output of the SBD was connected to a multichannel scaler (MCS), which recorded the number of pulses as a function of time [Fig. 3(b)]. The DR rate coefficient was determined from

$$R = \frac{dN}{dt} \frac{v_e v_i e^2}{I_e I_i} \frac{\pi r_e^2}{l^2}, \quad (7)$$

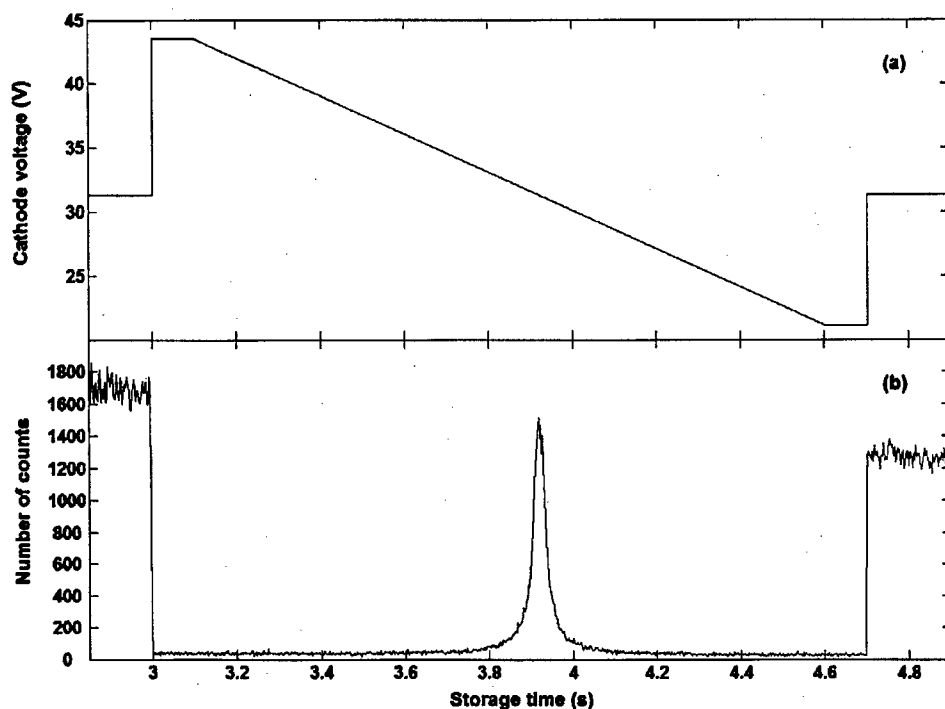


FIG. 3. (a) Electron cooler cathode voltage vs time. (b) The corresponding DR count rate.

where dN/dt is the count rate, v_e and v_i are the mean electron and ion velocities, I_e and I_i are the electron and ion beam currents, r_e is the electron beam radius, and l is the electron cooler length.

Since a value of the measured DR rate coefficient is the velocity weighted cross section averaged over the electron velocity distribution,²⁵ a Fourier transformation procedure is applied to extract the cross section.²¹ This method is efficient for low collision energy, because it takes into account the velocity spread of electrons. However, for the interaction energies in this study the velocity spread is negligible, which makes it appropriate to use the following formula to calculate the cross section:

$$\sigma_{\text{eff}} = \frac{R}{v_{cm}}, \quad (8)$$

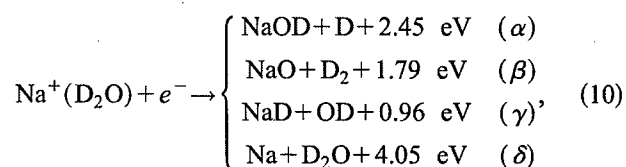
where $v_{cm} = \sqrt{2E_{cm}/m_e}$ is the electron velocity in the center-of-mass frame. The data were finally corrected for the space charge of the electron beam²⁶ and the effect of the toroidal magnetic field in the curved edges of the electron cooler.²⁷

The rate coefficient was obtained as a function of the electron temperature T_e by integrating the energy dependent cross section $\sigma(E_{cm})$ over the electron energy distribution:

$$\alpha = \frac{8\pi m_e}{(2\pi m_e k T_e)^{3/2}} \int_0^\infty E_{cm} \sigma(E_{cm}) e^{-E_{cm}/kT_e} dE_{cm}. \quad (9)$$

B. Branching ratios measurements

The following DR channels of $\text{Na}^+(\text{D}_2\text{O})$ are energetically accessible at an interaction energy of 0 eV:



where the energies correspond to particles that are in the ground states and correspond to the H isotopes. Isotopic shifts are small compared to the overall exothermicities and are not important to the present discussion, so have not been calculated. It is interesting to note that the recombination energy of this ion is low enough so that there are no exothermic channels available to produce three neutrals.

Since neutral particles arising from the same recombination event reached the detector essentially simultaneously, they gave rise to a signal proportional to the full beam energy E_b , which made it impossible to distinguish between events originating from the different dissociation channels. In order to overcome this problem, a 50 μm thick metal foil grid with 70 μm holes was inserted in front of the detector. The transmission of the grid is $P = 0.297 \pm 0.015$. Since some of the particles were stopped by this grid, the spectrum from the MCA showed a series of peaks corresponding to the recombination products. For instance, the products from each channel could be either detected with the probability P^2 at the full beam energy or with the probability $P(1-P)$ at the energy carried by an individual particle. Figure 4(a) shows the MCA spectrum recorded at a collision energy of nominally 0 eV. Fragments originating from background collisions also contributed to the peaks and a spectrum was also recorded at an interaction energy of 1 eV, where recombination is negligible, see Fig. 4(b). At this energy only residual gas collisions are considered to give rise to a signal. There is no full ion beam energy signal in this spectrum, ensuring that

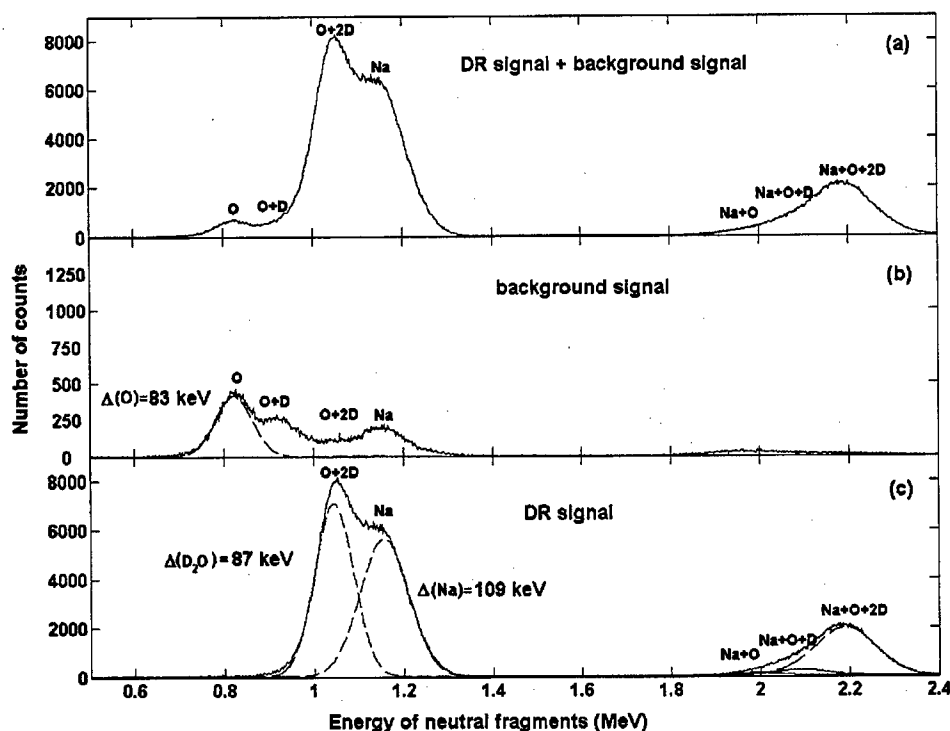


FIG. 4. (a) The signal from $\text{Na}^+(\text{D}_2\text{O}) + e^-$, measured at 0 eV interaction energy. (b) Background spectrum recorded at 1 eV interaction energy. (c) Background subtracted spectrum showing only DR at 0 eV interaction energy. Dashed lines represent Gaussian fits, corresponding to the different fragments.

electron capture from the residual gas is negligible. The background subtracted DR spectrum is shown in Fig. 4(c) after normalization to the total beam intensity during each collection run. It is seen that the Na peak is broader than the D_2O peak [Fig. 4(c)], even though the corresponding fragment energies are similar. However, the resolution of the D_2O signal is related to the energy spreads of the O and D signals via a quadratic sum, and from the fitting [Figs. 4(b) and 4(c)] it can be concluded that the width of the D_2O peak is mostly determined by the O contribution. The integrated intensities of the peaks are similar.

The contribution from each DR channel, N_α , N_β , N_γ , and N_δ , to the amount of the observed fragments, $A_{\text{D}_2\text{O}}$, A_{Na} , A_{NaO} , and $A_{\text{NaD}_2\text{O}}$, can be related through a set of linear equations:

$$\begin{bmatrix} A_{\text{D}_2\text{O}} \\ A_{\text{Na}} \\ A_{\text{NaO}} \\ A_{\text{NaOD}} \\ A_{\text{NaD}_2\text{O}} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & P(1-P) \\ 0 & 0 & 0 & P(1-P) \\ 0 & P(1-P) & 0 & 0 \\ P(1-P) & 0 & 0 & 0 \\ P^2 & P^2 & P^2 & P^2 \end{bmatrix} \times \begin{bmatrix} N_\alpha \\ N_\beta \\ N_\gamma \\ N_\delta \end{bmatrix} \quad (11)$$

The branching fractions n_α , n_β , n_γ , and n_δ were determined after normalization:

$$n_{\alpha,\beta,\gamma,\delta} = \frac{N_{\alpha,\beta,\gamma,\delta}}{N_\alpha + N_\beta + N_\gamma + N_\delta} \quad (12)$$

In order to determine the signal levels for use in the left side of Eq. (11), the number of counts of each fragment was determined by fitting the data to Gaussian curves [Fig. 4(c)].

IV. RESULTS AND DISCUSSION

A. Cross section and rate coefficient

The measured cross sections for DR of $\text{Na}^+(\text{D}_2\text{O})$ as a function of center-of-mass energy ranging from about 1 meV to 0.1 eV are shown in Fig. 5, where error bars represent statistical uncertainty. The systematic uncertainty corresponding to the most significant errors, viz., error in the elec-

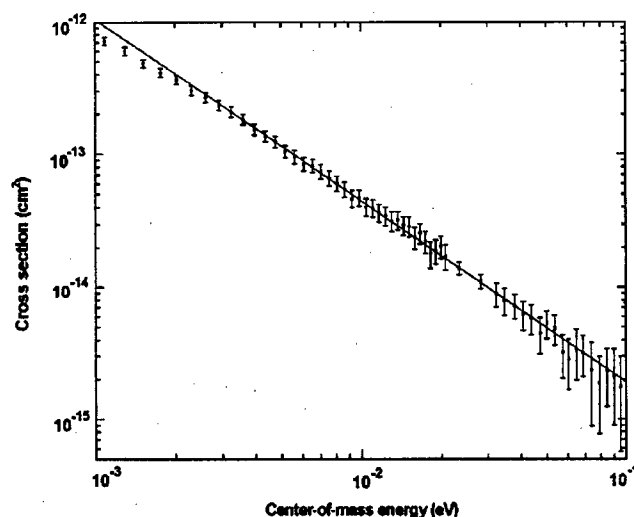


FIG. 5. Cross section for dissociative recombination of $\text{Na}^+(\text{D}_2\text{O})$ as a function of center-of-mass energy (solid squares with error bars). Solid line shows the best-fit data [Eq. (13)].

tron cooler length, ion and electron currents, was estimated to be 20%. A least-square power law fit is shown as a solid line in Fig. 5. The equation is

$$\sigma(E_{cm}) = (8.15 \pm 1.63) \times 10^{-17} E_{cm}^{-1.37 \pm 0.01} \text{ cm}^2. \quad (13)$$

The cross section dependence is steeper than E_{cm}^{-1} characteristic of the direct dissociative recombination mechanism.²⁸ The same tendency has been observed previously for other polyatomic ions.^{29,30}

Rate coefficients for thermal distributions of electrons have been calculated for electron temperatures from 50 K to 1000 K, which can be fitted by the equation

$$\alpha = (2.3 \pm 0.32) \times 10^{-7} \left(\frac{T_e}{300} \right)^{-0.95 \pm 0.01} \text{ cm}^3 \text{ s}^{-1}. \quad (14)$$

The observed temperature dependence differs from the $T_e^{-0.5}$ dependence predicted by Bardsley³¹ when only the direct DR mechanism is taken into account. This indicates that DR of the Na⁺(D₂O) ion is occurring in part by the indirect mechanism, which proceeds through vibrationally excited Rydberg states after the electron has been captured by the molecular ion.

It is interesting to compare the present results to those found for hydronium ions, H₃O⁺(H₂O)_n. Throughout the DR studies of water clusters with an H₃O⁺ core,^{32–34} the rate coefficients have been measured to be appreciably higher than found in the present study. Estimates of the H₃O⁺(H₂O)_n DR rate constants at 300 K are (0.5+2*n*) × 10^{−6} cm³ s^{−1} for *n* from 1 to 4; much larger than those found here. For the bare ion, D₃O⁺, which has the same number of atoms as Na⁺(D₂O), cross sections are larger by a factor of 2.5 to 3 than found here. This is probably related to the fact that recombination energy of H₃O⁺ is much larger than for Na⁺(H₂O). However, the electron energy dependence is almost identical at $E^{-1.46}$.

B. Branching ratios

The following branching ratios for the DR of Na⁺(D₂O) at 0 eV interaction energy were determined by solving Eq. (11) and normalizing the results Eq. (12):

$$\begin{aligned} n_\alpha(\text{NaOD} + \text{D}) &= 0.05 \pm 0.01, \\ n_\beta(\text{NaO} + \text{D}_2) &= 0.03 \pm 0.01, \\ n_\gamma(\text{NaD} + \text{OD}) &= 0, \\ n_\delta(\text{Na} + \text{D}_2\text{O}) &= 0.92 \pm 0.03. \end{aligned} \quad (15)$$

The uncertainties in the branching ratios indicate the variation of the result when the uncertainties in the grid transmission and the fitting of the peaks were included.

The DR of the Na⁺(D₂O) ion is a two-body dissociation process tending to break the weak Na⁺–D₂O bond (≈92% of the total reactivity) which as shown in Fig. 2, is more than twice as long as the O–H bonds. A DR study of the D⁺(D₂O)₂ cluster found similar results, where the cluster bonds break almost exclusively.³⁵ Channels α and β producing a D atom and a D₂ molecule, respectively, require one and two D–O bonds to be broken. These channels account for only 8% of all DR events, indicating that the covalent

bonds are harder to break than the Na⁺–D₂O ionic cluster bond. Of the two channels where covalent bonds are broken, simple bond fission is 70% more prevalent than the channel that breaks two bonds and forms another. The D₂ forming channel may involve a concerted mechanism where both of the O–D bonds break simultaneously as the D₂ bond is formed and would be expected to be enhanced by bending excitation in the D₂O molecule.

The channel γ does not contribute to the total reactivity. The confirmation that channel γ is absent follows from the background subtracted pulse-height spectrum [Fig. 4(c)], where contributions to NaD and OD signals are negligible. Thus, the order of importance of the dissociation channels follows simple chemical intuition. The descriptions of the chemical nature of the reaction can be described in decreasing order of importance as (1) breaking a weak ionic cluster bond, (2) breaking one covalent bond, (3) breaking two bonds and making another, and (4) rearrangement.

C. Kinetics of the chaperone mechanism

The rate expressions for Na⁺ and Na⁺(H₂O) in the chaperone mechanism are

$$\frac{d[\text{Na}^+]}{dt} = -k_f[\text{Na}^+][\text{H}_2\text{O}][M] + k_r[\text{Na}^+(\text{H}_2\text{O})][M], \quad (16)$$

$$\begin{aligned} \frac{d[\text{Na}^+(\text{H}_2\text{O})]}{dt} &= k_f[\text{Na}^+][\text{H}_2\text{O}][M] - k_r[\text{Na}^+(\text{H}_2\text{O})] \\ &\quad \times [M] - \alpha[\text{Na}^+(\text{H}_2\text{O})][e^-], \end{aligned} \quad (17)$$

where k_f and k_r are the forward and reverse rate coefficients for reaction (2), respectively, and square brackets are used to denote concentrations. Two simple limits can be described for loss of Na⁺. The first is if the effective dissociation rate constant $\alpha[e^-]$ is much larger than the effective reverse rate constant $k_r[M]$ and the second is vice versa. In the first case the rate for Na⁺ is given by the rate of clustering, i.e., as soon as the cluster forms it recombines with electrons. In this limit,

$$\frac{d[\text{Na}^+]}{dt} = -k_f[M][\text{H}_2\text{O}][\text{Na}^+], \quad (18)$$

where k_f has been measured in He.^{15,36} For the atmospheric gases, the clustering rate is expected to be about twice that for He and is given as³⁷

$$k_f = 9.5 \times 10^{-30} \left(\frac{300}{T_e} \right)^{1.5} \text{ cm}^6 \text{ s}^{-1}. \quad (19)$$

For the second limit the rate expression is written as

$$\frac{d[\text{Na}^+]}{dt} = -K_{eq}\alpha[\text{H}_2\text{O}][e^-][\text{Na}^+]. \quad (20)$$

K_{eq} is the equilibrium constant for Eq. (2). The value versus temperature is

$$K_{eq} = 1.36 \times 10^{-22} T_e \exp \left(\frac{\Delta S}{R} - \frac{\Delta H}{RT_e} \right) \text{ cm}^3, \quad (21)$$

where R is the molar gas constant, and ΔS and ΔH are the entropy and enthalpy changes,³ which are deemed to be weak functions of temperature.^{3,38}

With the above expressions, it is straightforward to calculate lifetimes for atmospheric conditions with respect to each of the three processes in the chaperone mechanism. Since the atmosphere is cold and the $\text{Na}^+ - \text{H}_2\text{O}$ bond relatively strong, decomposition can be ignored. Using standard atmospheric conditions, one finds clustering times on the order of $(1-5) \times 10^5$ s at 80–85 km, near the peak of the Na^+ layer.³⁹ Higher altitudes have even longer lifetimes. In this region, the electron concentration varies between $\approx 10^3$ and $10^5 \text{ e}^-/\text{cm}^3$. This translates into lifetimes between 3000 and 30 s, respectively. Comparing the two lifetimes shows that clustering is rate determining. Since pressure and water concentrations increase with decreasing altitude, this trend would reverse for the same electron concentrations below 60 km. However, in the natural atmosphere electrons quickly form negative ions at that altitude, so that recombination would be mostly ion-ion.⁴⁰

It is of course worth comparing the chaperone mechanism to three-body recombination involving Na^+ . There are no good measurements for Na^+ three-body recombination. Therefore we estimate the rate constant to be that found in CaO and Johnsen,⁴¹ which agreed well with theoretical calculations from Bates and Khare.⁴² At 200 K, the rate constant is $\sim 2 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. Using the parameters described above, the lifetime at 85 km is 3×10^7 s for an electron density of 10^5 cm^{-3} . Longer lifetimes apply for smaller electron densities. Thus, while the rate constant is larger for three-body recombination, the greater water vapor density leads to a faster loss process by clustering than by three-body recombination.

V. CONCLUSIONS

We have shown that the DR of the $\text{Na}^+(\text{D}_2\text{O})$ ion is an efficient process. The cross section was measured over collision energies ranging from 1 meV to 0.5 eV and shows a $E^{-1.37}$ dependence. The DR rate coefficient was deduced to follow $(2.3 \pm 0.32) \times 10^{-7} (T_e/300)^{-0.95 \pm 0.01} \text{ cm}^3 \text{ s}^{-1}$, indicating the presence of the indirect mechanism. Rate coefficients for a chaperone mechanism have been calculated for limiting values. The complete branching ratios were determined at the minimum center-of-mass energy. The $\text{Na}^+(\text{D}_2\text{O})$ ions dissociate only into two neutral fragments and $\text{Na} + \text{D}_2\text{O}$ channel is the most dominant (92%).

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- ¹ P. Soldán, V. Spirko, E. P. F. Lee, and T. G. Wright, *J. Chem. Phys.* **111**, 3420 (1999).
- ² E. P. F. Lee, P. Soldán, and T. G. Wright, *Chem. Phys. Lett.* **301**, 317 (1999).
- ³ I. Džidić and P. Kebarle, *J. Phys. Chem.* **74**, 1466 (1970).
- ⁴ A. W. Castleman, K. I. Peterson, B. L. Upschulte, and F. J. Schelling, *Int. J. Mass Spectrom. Ion Phys.* **47**, 203 (1983).
- ⁵ C. W. Bauschlicher, S. R. Langhoff, H. Partridge, J. E. Rice, and A. Komornicki, *J. Chem. Phys.* **95**, 5142 (1991).
- ⁶ E. Magnusson, *J. Phys. Chem.* **98**, 12558 (1994).
- ⁷ D. Feller, E. D. Woon, and M. W. Feyereisen, *J. Chem. Phys.* **103**, 3526 (1995).
- ⁸ E. D. Glendening and D. Feller, *J. Phys. Chem.* **99**, 3060 (1995).
- ⁹ T. N. Truong and E. V. Stefanovich, *Chem. Phys. Lett.* **256**, 348 (1996).
- ¹⁰ A. Tongraar, K. R. Liedl, and B. M. Rode, *J. Phys. Chem.* **102**, 10340 (1998).
- ¹¹ L. M. Ramaniah, M. Bernasconi, and M. Parrinello, *J. Chem. Phys.* **109**, 6839 (1998).
- ¹² M. Remko and M. Šarišský, *Chem. Phys. Lett.* **282**, 227 (1998).
- ¹³ P. D. Lyne, M. Hodoscek, and M. Karplus, *J. Phys. Chem.* **103**, 3462 (1998).
- ¹⁴ P. Soldán, E. P. F. Lee, S. D. Gamblin, and T. G. Wright, *Chem. Phys. Lett.* **313**, 379 (1999).
- ¹⁵ R. Johnsen, H. L. Brown, and M. A. Biondi, *J. Chem. Phys.* **55**, 186 (1971).
- ¹⁶ E. E. Ferguson, F. C. Fehsenfeld, and D. L. Albritton, in *Gas Phase in Chemistry*, edited by M. T. Bowers (Academic, San Diego, 1979), Vol. 45, p. 45.
- ¹⁷ R. S. Narcisi and A. D. Bailey, *J. Geophys. Res.* **70**, 3687 (1965).
- ¹⁸ P. P. Batista, B. R. Clemesha, I. S. Batista, and D. M. Simonich, *J. Geophys. Res.* **94**, 15349 (1989).
- ¹⁹ S. C. Collins, J. M. C. Plane, M. C. Kellay et al., *J. Atmos. Sol.-Terr. Phys.* **64**, 845 (2002).
- ²⁰ R. S. Narcisi and W. Roth, *Adv. Electron. Electron Phys.* **29**, 79 (1970).
- ²¹ C. Strömholm, J. Semaniak, S. Rosén, H. Danared, S. Datz, W. van der Zande, and M. Larsson, *Phys. Rev. A* **54**, 3086 (1996).
- ²² R. A. Perry, B. R. Rowe, A. A. Viggiano, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, *Geophys. Res. Lett.* **7**, 693 (1980).
- ²³ A. Simonsson, *Nucl. Instrum. Methods Phys. Res. A* **284**, 264 (1989).
- ²⁴ H. Danared, A. Källberg, G. Andler et al., *Nucl. Instrum. Methods Phys. Res. A* **441**, 123 (2000).
- ²⁵ H. Danared, G. Andler, L. Bagge et al., *Phys. Rev. Lett.* **72**, 3775 (1994).
- ²⁶ G. Kilgus, D. Habs, D. Schwalm, and A. Wolf, *Phys. Rev. A* **46**, 5730 (1992).
- ²⁷ A. Lampert, A. Wolf, D. Habs, J. Kettner, G. Kilgus, D. Schwalm, M. S. Pindzola, and N. R. Badnell, *Phys. Rev. A* **53**, 1413 (1996).
- ²⁸ E. P. Wigner, *Phys. Rev.* **73**(9), 1002 (1948).
- ²⁹ A. Neau, A. Al Khalili, S. Rosén et al., *J. Chem. Phys.* **113**, 1762 (2000).
- ³⁰ J. Semaniak, B. F. Minaev, A. M. Derkach et al., *Astrophys. J., Suppl. Ser.* **135**, 275 (2001).
- ³¹ J. N. Bardsley, *J. Phys. B* **1**, 365 (1968).
- ³² M. T. Leu, M. A. Biondi, and R. Johnsen, *Phys. Rev. A* **7**(1), 292 (1973).
- ³³ R. Johnsen, *J. Chem. Phys.* **98**, 5390 (1993).
- ³⁴ R. Johnsen, *J. Chem. Phys.* **98**, 5390 (1993).
- ³⁵ M. B. Nægård, J. B. C. Pettersson, A. M. Derkach et al., *J. Chem. Phys.* **117**, 5264 (2002).
- ³⁶ D. N. Smith, N. G. Adams, and E. Alge, *Astrophys. J.* **272**, 365 (1983).
- ³⁷ Y. Ikezoe, S. Matsuoka, M. Takebe, and A. Viggiano, 1987, *Gas Phase Ion-Molecule Reaction Rate Constants* (Tokyo: Ion Reactions Research Group of The Mass Spectrometry Society of Japan, 1986).
- ³⁸ E. S. Richter and C. F. Sechrist, Jr., *J. Atmos. Terr. Phys.* **41**, 576 (1979).
- ³⁹ A. S. Jursa, *Handbook of Geophysics and the Space Environment* (National Technical Information Service, Springfield, VA, 1985).
- ⁴⁰ A. A. Viggiano and F. Arnold, in *Atmospheric Electrodynamics*, edited by H. Volland (CRC, Boca Raton, FL, 1995), Vol. 1.
- ⁴¹ Y. S. Cao and R. Johnsen, *J. Chem. Phys.* **94**, 5443 (1991).
- ⁴² D. R. Bates and S. P. Khare, *Proc. Phys. Soc. Jpn.* **85**, 231 (1965).